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DEVELOP AN OPERATIONAL SYSTEM FOR EVALUATING AND TESTING METHODS AND INSTRUMENTS FOR DETERMINING THE EFFECTS OF FUELS AND FUEL ADDITIVES ON AUTOMOBILE EMISSIONS

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Causes of observed weight variations in collected particulates from automobile exhaust were sought. Chemical and physical properties of unused glass fiber filters were studied, and some chemical analyses of collected exhaust particulates were performed. No clear indication of a single cause for the variations could be discerned. An extensive statistical analysis of data obtained from additional experiments is suggested as a means of pinpointing the causes of the weight variations.

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Develop an Operational System for Evaluating and Testing Methods and Instruments for Determining the Effects of Fuels and Fuel Additives on Automobile Emissions

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MANAGEMENT SUMMARY

Contract No. 68-02-0324

"Develop an Operational System for Evaluating and Testing Methods and Instruments for Determining the Effects of Fuels and Fuel Additives on Automobile Exhaust Emissions".

Objective of Research

The original objective of this program, given in the title, was changed to a study of the behavior of glass filters used to collect particulate matter from automobile exhaust.

Significance of Research to Date

The weights of particulates collected from auto exhaust emissions showed unacceptable variations within lots, among filter types, and among filters from different manufacturers.

Data presented in this report show that the weight variations are real, and that they are related to automobile exhaust particulate collections rather than to particulate collections in general. Possible physical and chemical causes of these variations were studied, but no clear cause or causes were identified positively. The evidence presented indicates that the causes may be more subtle than originally suspected, and that their identification will require extensive statistical analysis of experimental data.

Application of Research Results

Until the causative factors of weight variations are identified, reproducible data are most likely to be obtained by tight controls over all known variables, including the exclusive use of glass filters from a specific manufacturing lot.

Goals For Next Period

No further work is scheduled under the present contract. Specific suggestions for additional work are given in the "Future Work" section of this report.

ABSTRACT

Causes of observed weight variations in collected particulates from automobile exhaust were sought. Chemical and physical properties of unused glass fiber filters were studied, and some chemical analyses of collected exhaust particulates were performed. No clear indication of a single cause for the variations could be discerned. An extensive statistical analysis of data obtained from additional experiments is suggested as a means of pinpointing the causes of the weight variations.

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DEVELOP AN OPERATIONAL SYSTEM FOR EVALUATING AND TESTING METHODS AND INSTRUMENTS FOR DETERMINING THE EFFECTS OF FUELS AND FUEL ADDITIVES ON AUTOMOBILE EXHAUST EMISSIONS

by

E. R. Blosser and J. F. Foster

INTRODUCTION

The initial purpose of this research program was to "develop an operational system for evaluating and collaboratively testing methods proven applicable to the measurement of the influence of fuels and fuel additives on vehicle emissions".(1) As the project progressed, various difficulties emerged that prevented the successful pursuit of the original goal. Therefore, a change in objective was discussed and agreed upon with the project monitor. The revised objective, briefly stated, was to "develop an understanding of the critical properties and characteristics of such filters which will contribute to the precision and reproducibility of measurements of the particulate loading of automobile emissions".(2)

Four principal sections comprise this report: first, the work (primarily a literature search) performed under the original scope of work; second, the experimental work to establish the nature and magnitude of the problem; third, the experimental work with different filters in an attempt to discover the reason(s) for variations; and fourth, recommendations for future work.

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(1) Scope of work, negotiated Contract 68-02-0324.

(2) Introduction, Twelfth Monthly Report, Contract 68-02-0324 (May 8, 1972).

OVERALL PROGRESS

Literature Survey

One of the initial tasks of this program was to identify fuels and fuel additives used in automobiles, and the means employed to measure their effect upon particulate emissions in the exhaust. A literature search was conducted, using a list of key words likely to identify articles relevant to the subject. Over 1,000 references were located and partially indexed and abstracted, and reprints or copies of the more pertinent ones were obtained. In this mass of literature very little was found dealing directly with fuels, fuel additives, and resulting automobile exhaust particulate emissions. Specifically, particulate collection schemes were not discussed, nor were compositions given for fuel additives. Further, it proved not practical for EPA to supply information on additive compositions, and a few direct inquiries to manufacturers produced no information. These formulations appear to be held securely as proprietary information and efforts to analyze fuels for the additives' compositions would have been beyond the scope of this program. For these reasons, with the agreement of the project monitor, the program was redirected toward an understanding of particulate filtration of particulate generated from nonleaded fuel.

Experimental Collections

As redefined, the immediate goal of this program became a study of glass fiber filters used to collect automobile exhaust particulate matter. Simply stated, not all filters give the same net weight of exhaust particulate matter even though the collections are made under identical conditions. The variations are not merely

random, nor can they be attributed to the several inherent errors of such collections. The variations are real in the sense that they can be reproduced, as is shown in the next sections.

Filters Used. For this study six different types of filters were obtained. Five of these are glass fiber; one was made of quartz fibers. One glass filter had an organic binder, not present in the other five. One filter was considerably thicker than the others. All filters were either received as 47-mm-diameter precut disks or were cut in our laboratory from sheet or roll stock to 47-mm-diameter disks.

The complete identification of the filters is as follows.

Whatman GF/A (No Lot No.) Box 1[(a)]
Box 2
Whatman GF/B (No Lot No.) Box 1[(a)]
Box 2
Gelman Type A Batch 8170
Batch 3172
Gelman Type E Lot 8168 Box 1[(a)]
Box 2
Mine Safety Appliance CT 75428, Lot J 7020
(47-mm-diameter disks cut from 8 x 10-inch sheets)
Pallflex Tissuequartz Style 2500 QAO, QC No. C-14581
(47-mm-diameter disks cut from 65-foot roll)

(a) Used in experiments where samples were taken from only one box. Box 1 and 2 are arbitrary numbers assigned to two boxes of the same lot number.
Whatman: Manufactured by W & R Balston, Ltd., England.
Gelman: Manufactured by Gelman Instrument Company, Ann Arbor, Michigan.
Mine Safety Appliance: Manufactured by Mine Safety Appliances Company, Pittsburgh, Pa.
Tissuequartz: Manufactured by Pallflex Products Corp., Putnam, Connecticut.

Automobile Exhaust Particulate Collection

The key experiments of this program were the collections made from diluted automobile exhaust and from ambient air. For these experiments the automobile and associated equipment were those purchased and used on another project and were used with the Sponsor's permission. The automobile is a 1970 Ford with a 351-cubic-inch engine and automatic transmission. The automobile was run on a chassis dynamometer under tape-controlled Los Angeles cycles. Each run consisted of 8 L.A.-4 cycles, begun after initial warm up; no forced engine cooling was done between cycles. The fuel was a nonleaded research fuel, RE 141-B, supplied by the Coordinating Research Council, the co-sponsor of the project associated with the automobile. The engine exhaust was diluted approximately 20:1 with filtered ambient air forced into a 2-foot-diameter stainless steel dilution tunnel maintained at an excess pressure above ambient of 1 inch of water. Sampling was performed at a position about 30 feet beyond the dilution point, using 13 collection points in a plane perpendicular to and within the dilution tunnel. See Figure 1 for the arrangement of the sampling inlets in the tunnel. The relative humidity (R.H.) at this point was approximately 50 percent at 95 to 105 F. The flow through each filter was controlled by calibrated critical flow orifices set for 0.50 cfm. A large mechanical vacuum backing pump maintained the lines downstream of the orifices at about 22-inches Hg negative pressure (200 Torr).

Before beginning each run, the filters to be used were allowed to equilibrate for at least 1 hour in the constant temperature and humidity weighing room (74 F, 54 percent R.H.). After weighing the filters to ± 1 μg, they were installed in the holders and the run was begun. About 3 hours of operation, equivalent to about 61 miles, were required to complete the 8 L.A. cycles. Upon completion of each run, the filters were removed from the holders and equilibrated in the constant temperature-humidity

room before reweighing. No evidence of weight drift, ± 1 μg, suggested that equilibration in the weighing room was reasonably complete under these conditions.

The weights of the collected particulate matter from the first run are given in Table 1. Duplicates of each of six filter types were used (triplicates of the MSA filter), with agreement between replicates ranging from good to poor. Among types, the agreement was not satisfactory; indeed, this lack of agreement is the subject of this study. Two types were below the overall average weight gain (Whatman GF/A and Tissuequartz); two were "average" (Gelman Type E and MSA); and two were "high" (Whatman GF/B and Gelman Type A).

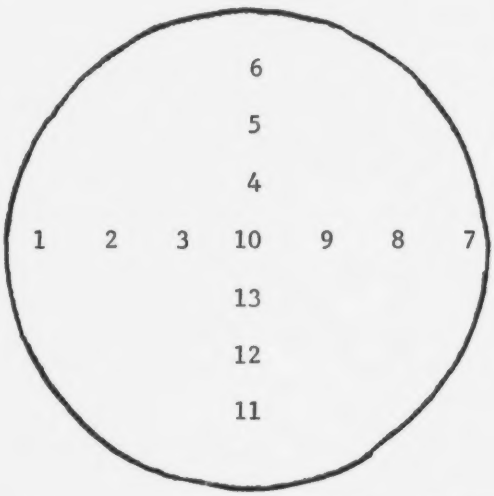

FIGURE 1. SAMPLING PORT LOCATIONS, LOOKING TOWARD AUTOMOBILE

(Numbers are the filter locations mentioned in the text and tables.)

An insufficient number of each type of filter prevented reasonably confident conclusions to be drawn from this single run. Therefore, the experiment was repeated to improve the satistical reliability of the data. For subsequent runs, the MSA filter was arbitrarily chosen as the reference filter. Three runs were made using the same automobile and tunnel conditions

TABLE 1. SUMMARY OF COLLECTIONS ON GLASS FILTERS

Filter Type	Automobile Exhaust: Run No. (Table No.)	Number of Filters	Percent Avg. Dev.[a]	Ratio[b], Type MSA	Ambient Air: Run No. (Table No.)	Number of Filters	Percent Avg. Dev.[a]	Ratio[b], Type MSA
Whatman GF/A	1 (2)	2	[6.2]	0.69	2 (8)	10	14.4	0.97
Ditto	3 (4)	4	7.4	0.56				
"	5 (6)	5	14.8	0.48				
Whatman GF/B	1 (2)	2	[36.]	1.66	3 (9)	7	2.1	0.95
Ditto	3 (4)	5	12.9	0.90				
Gelman Type A	1 (2)	1	-	1.74	4 (10)	10	7.1	1.08
Ditto	4 (5)	4	10.0	0.74				
Gelman Type E	1 (2)	2	[0.36]	1.06	5 (11)	10	3.6	1.03
Ditto	4 (5)	5	6.2	0.91				
Tissuequartz	1 (2)	1	-	0.45	6 (12)	10	12.1	1.07
Ditto	5 (6)	5	2.4	Minus Value				
MSA	1 (2)	3	[21.2]	-	1 (7)	9	10.0	-
Ditto	2 (3)	12	12.9	-	2 (8)	3	11.7	-
"	3 (4)	3	7.4	-	3 (9)	3	3.3	-
"	4 (5)	3	10.0	-	4 (10)	3	10.7	-
"	5 (6)	3	3.9	-	5 (11)	3	10.0	-
"					6 (12)	3	1.5	-
		Averages 8.8					7.9	

[ ] Excluded from computation of average (see page 20).

(a) Percent average deviation = $\frac{\Sigma|\bar{wt} - wt|}{\frac{n}{\bar{wt}}} \times 100$

(b) Ratio = $\frac{\text{average weight of particulate collected on given filter type}}{\text{average weight of particulate collected on MSA filters during same run}}$

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as described. In each run three MSA filters were randomly located in the holders, and five each of two other filter types. Weighing was done in the constant humidity-temperature room with at least 1 hour equilibration. The detailed results of these runs are given in Tables 2 through 6, and are summarized in Table 1. More will be said about these runs later in this report, but first the ambient air collections will be described.

Ambient Air Particulate Collection

Ambient air collections of particulate matter were made using the same types of filters as were used for the automobile exhaust collections. The differences in conditions were:

(1) The automobile was not operating
(2) The blower supplying filtered ambient air to the dilution tunnel was not operating
(3) The sampling was conducted for longer times
(4) The temperature and humidity in the tunnel were ambient.

Apart from these necessary differences, all other conditions were as nearly identical as possible with the automobile exhaust collections. Thus, variables such as weighing errors, handling losses, humidity effects, etc. should be directly comparable in the two different sets of collections.

The details of ambient air collection data are given in Tables 7 through 12, and are summarized, with the automobile exhaust data, in Table 1.

One key point stands out in Table 1. This is the observed fact that (a) different filter types give different collected weights of automobile exhaust particulate matter, while (b) different filter types give the same weights of collected ambient air particulate matter. The disparity between the performance of, for example, Whatman GF/A filters and MSA filters when filtering automobile exhaust and when filtering ambient air is clear; it makes no difference, relatively, what reference base is chosen for data normalization. Therefore, it

seems evident that one or more of the following conditions exists for automobile exhaust collections and does not exist, or exists to a remarkably lesser extent, during ambient air collections.

(A) Assumption: The higher observed normalized automobile exhaust collections are most nearly correct. Therefore, lower normalized results indicate losses.

(1) Some exhaust particulates pass through some filters.

(2) Particulates are lost from some filters after collection.

(3) Exhaust gases weaken some filters and thus lead to mechanical handling losses.

(4) Exhaust gases remove from some filters materials present in these filters.

(5) Exhaust gases ablate bulk fibers from some filters.

(B) Assumption: The lower observed normalized automobile exhaust collections are most nearly correct. Therefore, higher normalized values indicate pickup.

(1) Some nonparticulate component(s) of exhaust are retained by some filters.

(2) Some component(s) of air are retained by some filters to an enhanced degree in the presence of exhaust.

TABLE 2. AUTO EXHAUST PARTICULATE COLLECTION ON GLASS FILTERS, RUN 1

Filter Type	Filter Location	Gain Per Filter, μg	Average μg	Ratio[(b)], Type MSA
Whatman GF/A, Box 1	10	288.	272.	0.69
	6	255.		
Whatman GF/B, Box 1	7	421.	655.	1.66
	8	890.		
Gelman Type A, Batch 8170	4	[1403.]	687.	1.74
	3	687.		
Gelman Type E, Box 1	2	419.	418.	1.06
	5	416.		
MSA	1	369.	395.	-
	13	520.		
	12	295.		
Tissuequartz	9	[55.][(a)]	180.	0.45
	11	180.		
Overall Average			431.	

[ ] Excluded from further computation.

(a) Filter torn upon removal from holder.

(b) Ratio = $\frac{\text{average weight of particulate collected on given filter type}}{\text{average weight of particulate collected on MSA filters during same run}}$

TABLE 3. AUTO EXHAUST PARTICULATE COLLECTION ON GLASS FILTERS, RUN 2

Filter Type	Filter Location	Gain Per Filter, μg	Average	Avg. Dev.(a)	Percent Avg. Dev.(b)
MSA	10	347			
Ditto	6	411			
"	7	407			
"	8	501			
"	4	451			
"	3	Lost	411	53.	12.9
"	2	335			
"	5	430			
"	1	345			
"	13	544			
"	12	300			
"	9	438			
"	11	422			
"	Blank	-16			
"	Blank	-23			

(a) Average deviation = $\frac{\Sigma \left| \bar{wt} - wt \right|}{n}$

(b) Percent average deviation = $\frac{\text{average deviation}}{\bar{wt}} \times 100$

TABLE 4. AUTO EXHAUST PARTICULATE COLLECTION ON GLASS FILTERS, RUN 3

Filter Type	Filter Location	Gain Per Filter, µg	Average	Avg. Dev.[a]	Percent Avg. Dev.[b]	Ratio[c], Type / MSA
MSA	2	287				
Ditto	8	360	324	24.	7.4	-
"	12	324				
"	Blank	3				
Whatman GF/A	5	181				
Ditto	9	[313]				
"	10	173	182	8.5	4.7	0.56
"	13	175				
"	11	199				
"	Blank	-33				
Whatman GF/B	1	304				
Ditto	3	263				
"	4	345	292	38.	12.9	0.90
"	7	224				
"	6	325				
"	Blank	-41				

[ ] Excluded from further calculation.

(a) Average deviation = $\frac{\Sigma \left| \bar{wt} - wt \right|}{n}$

(b) Percent average deviation = $\frac{\text{average deviation}}{\bar{wt}} \times 100$

(c) Ratio = $\frac{\text{average weight of particulate collected on given filter type}}{\text{average weight of particulate collected on MSA filters during same run}}$

TABLE 5. AUTO EXHAUST PARTICULATE COLLECTION ON GLASS FILTERS, RUN 4

Filter Type	Filter Location	Gain Per Filter, μg	Average	Avg. Dev.[a]	Percent Avg. Dev.[b]	Ratio[c], Type / MSA
MSA	8	363				
Ditto	2	272	315	32.	10.	-
"	12	311				
"	Blank	-9				
Gelman Type A	5	279				
Ditto	1	209				
"	13	220	233	23.	10.	0.74
"	7	225				
"	6	[752]				
"	Blank	-21				
Gelman Type E	4	301				
Ditto	3	257				
"	11	314	286	18.	6.2	0.91
"	9	279				
"	10	277				
"	Blank	-9				

[ ] Excluded from further calculation.

(a) Average deviation = $\frac{\Sigma \left| \bar{wt} - wt \right|}{n}$

(b) Percent average deviation = $\frac{\text{average deviation}}{\bar{wt}} \times 100$

(c) Ratio = $\frac{\text{average weight of particulate collected on given filter type}}{\text{average weight of particulate collected on MSA filters during same run}}$

TABLE 6. AUTO EXHAUST PARTICULATE COLLECTION ON GLASS FILTERS, RUN 5

Filter Type	Filter Location	Gain Per Filter, µg	Average	Avg. Dev.[a]	Percent Avg. Dev.[b]	Ratio[c], Type MSA
MSA	10	342				
Ditto	4	370	349	14.	3.9	-
"	13	336				
"	Blank	-33				
Tissuequartz	9	-62				
Ditto	5	-58				
"	7	-59	-59	1.4	2.4	Minus Value
"	6	-60				
"	8	-57				
"	Blank	-45				
Whatman GF/A	11	205				
Ditto	2	185				
"	3	166	167	25.	14.8	0.48
"	12	175				
"	1	106				
"	Blank	-38				

(a) Average deviation = $\frac{\Sigma \left| \bar{wt} - wt \right|}{n}$

(b) Percent average deviation = $\frac{\text{average deviation}}{\bar{wt}} \times 100$

(c) Ratio = $\frac{\text{average weight of particulate collected on given filter type}}{\text{average weight of particulate collected on MSA filters during same run}}$

TABLE 7. AMBIENT AIR COLLECTION ON GLASS FILTERS, RUN 1

Filter Type	Filter Location	Gain Per Filter, µg
MSA	1	403
Ditto	2	389
"	3	Lost
"	4	536
"	5	459
"	6	522
"	7	492
"	8	537
"	9	426
"	10	454
"	11	Lost
"	12	Lost
"	13	[766]
"	Blank	0
"	Blank	-10

Average - 468

Average deviation - 47

Percent average deviation - 10

23-hour collection (19.5 m^3 total per filter)

TABLE 8. AMBIENT AIR COLLECTION ON GLASS FILTERS, RUN 2

Filter Type	Filter Location	Gain Per Filter, μg
MSA	2	406
Ditto	8	561
"	12	465
"	Blank	-23

Average - 477
Average deviation - 56
Percent average deviation - 11.7

Whatman GF/A	1	418
Ditto	3	403
"	4	529
"	5	550
"	6	365
"	7	386
"	9	514
"	10	594
"	11	426
"	13	449
"	Blank	-32

Average - 463
Average deviation - 67
Percent average deviation - 14.4

Ratio, $\frac{\text{Whatman GF/A}}{\text{MSA}}$ - 0.97

23-hour collection (= 19.5 m^3 total per filter)

TABLE 9. AMBIENT AIR COLLECTION ON GLASS FILTERS, RUN 3

Filter Type	Filter Location	Gain Per Filter, μg
MSA	1	727
Ditto	6	665
"	7	705
"	Blank	5
Average - 699		
Average deviation - 23		
Percent average deviation - 3.3		
Whatman GF/B	2	654
Ditto	3	636
"	4	666
"	5	658
"	8	702
"	9	664
"	10	651
"	11	[255]
"	12	[215]
"	13	[227]
"	Blank	-38
Average - 662		
Average deviation - 14		
Percent average deviation - 2.1		

Ratio, $\frac{\text{Whatman GF/B}}{\text{MSA}}$ - 0.95

[ ] Filter removed after 8.5 hours; value excluded from further calculation.

23.5-hour collection (= 20.0 m^3 total per filter)

TABLE 10. AMBIENT AIR COLLECTION ON GLASS FILTERS, RUN 4

Filter Type	Filter Location	Gain Per Filter, μg
MSA	1	565
Ditto	5	590
"	9	448
"	Blank	-30

Average - 534
Average deviation - 57
Percent average deviation - 10.7

Gelman Type A	2	483
Ditto	3	522
"	4	593
"	6	568
"	7	621
"	8	640
"	10	597
"	11	637
"	12	537
"	13	593
"	Blank	-20

Average - 579
Average deviation - 41
Percent average deviation - 7.1

Ratio, $\frac{\text{Gelman Type A}}{\text{MSA}}$ - 1.08

19-hour collection (= 16.2 m^3 total per filter)

TABLE 11. AMBIENT AIR COLLECTION ON GLASS FILTERS, RUN 5

Filter Type	Filter Location	Gain Per Filter, μg
MSA	2	806
Ditto	5	830
"	9	810
"	Blank	-3
Average - 815		
Average deviation - 10		
Percent average deviation - 1.2		
Gelman Type E	1	843
Ditto	3	795
"	4	798
"	6	815
"	7	830
"	8	856
"	10	873
"	11	872
"	12	799
"	13	891
"	Blank	4
Average - 837		
Average deviation - 30		
Percent average deviation - 3.6		
Ratio, $\frac{\text{Gelman Type E}}{\text{MSA}}$ - 1.03		
18.25-hour collection (=15.5 m^3 total per filter)		

TABLE 12. AMBIENT AIR COLLECTION ON GLASS FILTERS, RUN 6

Filter Type	Filter Location	Gain Per Filter, μg
MSA	4	1371
Ditto	8	1428
"	11	1392
"	Blank	1

Average - 1397
Average deviation - 21
Percent average deviation - 1.5

Tissuequartz	1	1349
Ditto	2	1257
"	3	1399
"	5	1671
"	6	1818
"	7	1351
"	9	1886
"	10	1448
"	12	1300
"	13	1438
"	Blank	-44

Average - 1492
Average deviation - 180
Percent average deviation - 12.1

Ratio, $\frac{\text{Tissuequartz}}{\text{MSA}}$ - 1.07

23.5-hour collection (= 20 m^3 total per filter)

Detailed Data Concerning the Automobile Exhaust and Ambient Air Particulate Collection Data. The detailed data that were summarized in Table 1 are presented in Tables 2 through 6 (automobile exhaust) and Tables 7 through 12 (ambient air exhaust). In each table the filter type, its location within the dilution tunnel (Figure 1), the measured weight gain or loss after collection, the average weight change for each type, and the precision statistics are given where applicable.

All averages are simple arithmetical averages, and all precision statistics ignore difference signs. Average deviations rather than standard deviations were used because the number of observations varies from run to run. The precision data using standard deviations are prejudiced against sets having fewer observations because the divisor is n-1, rather than n as is used here.

Filter location information is included to demonstrate the interchangability (equivalence) of the 13 locations. Where applicable, the data in Tables 1 and 2 have been corrected for an improper critical flow orifice. "Lost" data refer either to individual filters that were mechanically ruined upon removal from their holders, or (in Table 7) to a malfunction in part of the vacuum manifold.

Occasional data are excluded from computations. The cause of these abnormal values is not known. All precision data from Table 2 are neglected in further calculations; since there are only one or two observations for all but the MSA filters, it seemed best to discard all the precision data from that run.

Study of Filter Characteristics

Work reported in the preceding section confirms the observation by persons at EPA and elsewhere that not all glass fiber filters collect, uniformily and consistently, the particulates in automobile exhaust. In attempts to discover the causes of these observed variations the different filter types used in this study were subjected to various examinations, both physical and chemical.

Physical Properties

Physical properties can play an important role in the collection and retention of particles and in the handling characteristics of the filters. The properties studied and the results are described in the following sections.

Weight Uniformity. Variations of weight within a given type or lot of a manufacturer are one indication of uniformity or quality control. From each of the package units of the filters obtained for this study, random individual filters were weighed to the nearest 0.1 mg on a Cahn digital balance Model DTL. From 10 to 40 such weighings from each type or batch gave the data shown in Table 13. It is seen that the standard deviation of the weights of individual filters from a single package (lot, type, or batch) ranges from 1.13 mg to 3.86 mg per 47-mm-diameter filter. Repetitive weighings of the same filter, weighed to the nearest 0.01 milligram, gave a percent coefficient variation of 0.01. An interesting point is the difference in the standard deviations of 2 batches of the Gelman Type A filter. No other (known) different batches of a given type from a given manufacturer were used in the program so an "average" batch-to-batch variation cannot be established.

Thickness and Density. The thicknesses of ten samples of each filter type were measured using an Ames gage with a 1.25-inch-diameter foot and a pressure of 25 g (= 3.16 g/cm^2 = 0.718 oz/in^2). The results are shown in Table 14.

Abrasion Resistance. Any weight loss inadvertently caused by handling between the tare and the gross weighings will of course give a fictitiously low value for the collected particulate matter. Two methods were employed to assess possible losses by handling. The first method, insertion in and removal from the filter holder (Gelman Model 1235), with the 1-7/8-inch-OD rubber O-ring removed, was not a valid means for measuring differences. In this test the seal was formed between the metal screen and the mating wall, which is normally the internal support for the O-ring. The mating ring is free to turn on the filter during assembly.

TABLE 13. WEIGHT VARIATION OF GLASS FILTERS

	Whatman				Gelman					
	GF/A		GF/B		Type A		Type E		MSA	Tissue-quartz
	Box 1	Box 2	Box 1	Box 2	Batch 8170	Batch 8172	Box 1	Box 2	From 4 Sheets	From 65' Roll
Weight, milligrams, average	94.44	96.54	267.49	267.58	151.43	135.90	138.36	137.67	107.48	116.75
Range										
Low	92.3	93.9	263.8	262.6	148.3	128.4	134.7	134.1	105.3	114.4
High	96.8	98.6	271.7	271.7	155.5	141.4	141.3	141.2	108.2	119.3
σ(a)	1.38	1.39	2.20	2.50	2.35	3.86	1.81	1.95	1.13	1.61
Average σ	1.38		2.35				1.88			
ν(b)	1.45		0.88		1.55	2.84	1.36		1.05	1.38

(a) $\sigma = \sqrt{\frac{\Sigma(\bar{w} - w)^2}{n-1}}$.

(b) $\nu = \frac{\sigma}{\bar{w}} \times 100.$

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TABLE 14. THICKNESS MEASUREMENTS AND CALCULATED DENSITIES OF GLASS FILTERS.

	Weight			Thickness			Density
	per 47-mm diam. filter, mg	mg/cm^2	ν(a)	mil(b)	mm	ν(a)	g/cm^3
Whatman GF/A	94	5.4	1.45	15.0	0.38_0	3.2	0.14_2
WhatmanGF/B	267	15.4	0.88	37.8	0.96_1	1.7	0.16_0
Gelman Type A	151	8.7	1.55	27.6	0.70_2	2.5	0.12_4
Gelman Type E	138	7.9	1.36	31.0	0.78_7	2.3	0.10_1
MSA	107	6.2	1.05	17.0	0.43_2	3.1	0.14_3
Tissuequartz	117	6.7	1.38	23.3	0.59_2	1.8	0.11_4

(a) $\nu = \frac{\sigma}{\bar{x}} \times 100$, where $\sigma = \sqrt{\frac{(\bar{x} - x)^2}{n-1}}$

(b) Mil = 0.001 inch.

With care, no loss (to the nearest 0.1 mg) was observed in most cases for any filter; sporadically, gross amounts (milligrams) of filter were torn from a filter, but this event was usually preceded by allowing the mating ring to rotate during the tightening step. It was concluded that, although this test is not highly reliable, with reasonable care all but the Tissuequartz lost either nothing (<0.1 mg), or major amounts could be readily detected visually and thus were cause for rejecting that specific collection. The Tissuequartz did seem more prone to tearing even with careful handling.

The second evaluation for handling properties measured abrasion resistance. Samples of each filter were subjected to a "sieving" motion for 10-, 20-, and 40-minute periods, using new filters for each period. The results of this evaluation are presented in Table 15. The MSA and Tissuequartz filters lost amounts of material proportional to the length of agitation, but the Whatman and Gelman filter losses did not increase proportionally with increased time.

The agitation was provided by a Rotap® machine used to sieve samples of ore. The filters were placed, inlet side down, on a 1/8-inch opening sieve. The motion is horizontal; one side of the sieve moves back and forth in a straight line while the other side moves back and forth in a large arc perpendicular to the other horizontal motion. Simultaneously the assembly is tapped from above once per cycle; the frequency is about 120 cycles per minute. These motions probably ablate the filters far more severely than would any but very careless handling.

From the abrasion studies it was concluded that (a) normal handling with reasonable care should result in less than a 0.05-mg loss for any filter except Whatman GF/B; that type gave a 1-minute average loss of 0.1 mg; (b) losses

TABLE 15. ABRASION LOSS OF GLASS FILTERS
(Rotap Agitation)

	Whatman				Gelman					
					Type A					
	GF/A		GF/B		Batch	Batch	Type E			
	Box 1	Box 2	Box 1	Box 2	8170	8172	Box 1	Box 2	MSA	Tissue-quartz
Run 1 (10 min) Weight loss, mg	0.5	0.3	1.	2.	0.1	0.4	0.0	0.0	0.5	0.5
Run 2 (20 min) Weight loss, mg	0.4	0.1	1.	2.	0.1	0.3	0.0	0.0	0.7	0.8
Run 3 (40 min) Weight loss, mg	0.5	0.0	2.	2.	0.1	0.7	0.1	0.2	1.6	1.9
Average loss/min, mg	0.027	0.012	0.070	0.120	0.006	0.024	0.0008	0.002	0.042	0.044
Average loss/min, mg	0.020		0.100		0.015		0.001		0.042	0.044

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from insertion in and removal from the filter holder are either <0.1 mg or major, and visual inspection should be made to guard against the major losses. In any case, the data shown in Tables 7 through 12 suggest that abrasion losses, if they occur, at least are reproducible within a filter type to about ± 50 μg. That figure is the average total error of the ambient air experiments (8 percent of 600 μg), and includes possible errors from other causes in addition to ablative losses.

Pressure Differential. The pressure drop across the 47-mm filters was measured at a flow rate of 1.0 cfm, controlled by a calibrated critical flow orifice. The pressure differential was measured at a tee between the exit side of the filter and the limiting orifice using an open-end water manometer. The results, given in Table 16, show that all but the Whatman GF/B have pressure drops quite close to 18 inches of water; the GF/B is a much heavier and thicker filter than the others.

Humidity Effects. A significant contribution to the wide spread among observed weights of collected automobile exhaust particulate matter could be made by differences in adsorbed water on the filter. If different types of filters, or even different filters from the same lot, adsorbed varying amounts of water from the exhaust stream, these differences would be reflected in the measured weight changes attributed to particulate matter.

To measure the moisture effect two large desiccators were set up; one with Drierite® in the bottom part, the other with water. Two or more weighed samples of each filter type were placed on wire screens just above the Drierite or water and allowed to equilibrate at room temperature (72-74 F). After a time period ranging from overnight to one week, each filter was removed from the desiccator and placed on the recording balance pan. Within the enclosed

TABLE 16. PRESSURE DROP OF 47-mm[(a)] GLASS FILTERS

[Inches of water differential[(b)] at 1.0 cfm[(c)]]

	ΔP[(d)]	σ[(e)]	ν[(f)]
Whatman GF/A, Box 1	16.4	0.55	3.3
Whatman GF/A, Box 2	17.6	0.47	2.7
Whatman GF/B, Box 1	43.8	1.0	2.3
Whatman GF/B, Box 2	44.6	1.1	2.5
Gelman Type A, Batch 8170	21.7	1.9	8.8
Gelman Type A, Batch 8172	20.6	0.68	3.3
Gelman Type E, Box 1	18.5	0.28	1.5
Gelman Type E, Box 2	18.5	0.27	1.4
MSA	18.2	0.32	1.7
Tissuequartz	15.9	0.49	3.1

(a) Effective diameter = 35 mm = 1-3/8 inch = 9.62 cm^2 = 1.49 $in.^2$.

(b) 1 inch of water differential = 1.87 torr (mm Hg).

(c) 1 cfm = 0.0283 m^3/min.

(d) Average of ΔP determinations on 6 individual filters.

(e) $\sigma = \sqrt{\frac{\Sigma(\overline{\Delta P} - \Delta P)^2}{n-1}}$.

(f) $\nu = \frac{\sigma}{\Delta P} \times 100$.

volume of the balance pan was a small dish containing either Drierite or water. (Samples from the desiccator containing Drierite were weighed in the balance with water, and vice versa.) The transfer from the desiccator to the balance was accomplished as rapidly as possible (2 to 3 seconds), and the readings were begun immediately, since the balance requires only a few seconds to stabilize. Either 50 or 200 mg was tared from the balance so that the weighings could be made on the 100-mg full-scale range with a sensitivity of 0.1 mg. A few weighings were made with almost the entire filter weight tared out so that the balance could be set on the 10-mg full-scale range and read to 0.01 mg. The recorder was also set to higher sensitivity with the zero point depressed. Thus, it was possible to record very small weight changes, as was done for the chart in Figure 5. Since it is difficult to anticipate the weight of the filter closely enough to make all the necessary adjustments before removing the filter from the desiccator, quite a few experiments were aborted because an incorrect estimate was made, and the readings were off-scale.

The data from these experiments are shown in Table 17. The "ΔW" columns are the weight change of the filter while on the balance, and are the gain or loss upon a change in the relative humidity. The "Time to Constancy" columns are read from the chart recording and are the approximate time at which the rate of change becomes nearly zero. This estimate is somewhat subjective, but should be consistent from filter to filter. The "ΔW from 50 percent RH" column is the weight difference of the filter as weighed before placing it in the desiccator, and at the constancy point defined above.

TABLE 17. WEIGHT CHANGE OF GLASS FILTER AS A FUNCTION OF HUMIDITY(a)

Filter Sample	Dry to Wet			Wet to Dry		
	Total ΔW, mg	Time to Constancy, min	ΔW From ≈50% RH, mg	Total ΔW, mg	Time to Constancy, min	ΔW From ≈50% RH, mg
Whatman GF/A (Box 1)	0.1	[70]	-0.1	10.5	4	-0.8
	0.5	2	0.0	13.6	3	0.0
(Box 2)	0.1	~2	0.0	9.5	6	+0.2
	0.1	~2	-0.2	7.7	3	+0.1
Average	0.2	~2	-0.1	10.3	4	-0.1
Whatman GF/B (Box 1)	0.1	[15]	-1.0	4.0	6	+1.8
	0.3	~2	-0.8			
(Box 2)	0.0	--	+0.1	21.1	8	-0.3
	0.1	~2	-0.6			
Average	0.1	~2	-0.6	(13)	7	+0.7
Gelman Type A, Batch 8170	0.1	~2	-0.1	4.6	2	+0.2
				4.2	2	+0.4
Average	0.1	~2	-0.1	4.4	2	+0.3
Gelman Type A, Batch 8172	0.2	~2	-0.1	23.8	10	-4.8
	0.3	~2	-0.2	23.8	9	-0.2
Average	0.2	~2	-0.1	23.8	9	-2.5
Gelman Type E (Box 1)	0.4	~2	-0.3	12.8	6	-0.1
	0.3	~2	-0.1	10.3	7	-0.1
Average	0.3	~2	-0.2	11.5	6	-0.1
(Box 2)	0.2	~2	0.0	3.0	1	+0.2
	0.0	--	-0.1	1.1	1	+0.3
Average	0.1	~2	-0.1	2.0	1	+0.2
MSA	0.0	--	0.0	39.5	13	-0.1
	0.5	~2	-0.3	29.6	11	+0.1
	0.3	~2	-0.3	22.2	8	-0.5
				51.1	23	-0.2
Average	0.3	~2	-0.2	30.6	14	-0.2
Tissuequartz	2.2	52	-1.5	5.4	6	-0.5
	3.6	46	-1.6	4.5	8	-0.7
	4.1	60	-0.6			
	5.3	26	-0.4			
Average	3.8	46	-1.0	4.9	7	-0.6

(a) See text for explanation of terms.

[ ] Not included in average.

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Two facts are clear from the data. First, the loss of weight in going from the humid desiccator to the dry balance is far more noticeable than the reverse (dry to wet). Typical recorder plots of these changes are shown in Figure 2 through 6. Second, true equilibrium is not established within the balance enclosure. If true equilibrium were established, the gain in weight going from dry to wet should equal the loss in weight going from wet to dry. Only the Tissuequartz filter approximates this situation. It appears that most filters, whether from the dry or the wet atmospheres, rather quickly (<30 minutes) arrive at a weight close (± 0.1 to 0.2 mg) to that at ambient (50 percent) relative humidity. The additional weight gained in the wet atmosphere apparently is acquired over a much longer time period than the hour or less that the filter was on the balance. No measurement of nor control over the actual humidity in the balance was possible, and it is inferred that the R.H. in the balance is close to ambient (≈ 50 percent) when the weighing commences, because the cover was opened to insert the sample.

In retrospect, the experiment would be more meaningful if weight changes to ambient R.H. had been sought. The presence of Drierite or water under the balance cover did not establish equilibrium at high or low R.H. during the weighing period, but only introduced another (unknown) variable. In spite of that uncertainty, the differences among the filters should be valid qualitatively.

Results in Table 17 and Figures 2 and 3 show that the Tissuequartz equilibrates quite rapidly, either up or down. This can be interpreted to mean that the material is sensitive to humidity changes, and that Tissuequartz filters must be weighed under well controlled humidity conditions. Other differences shown in Table 17 are the marked variation between the

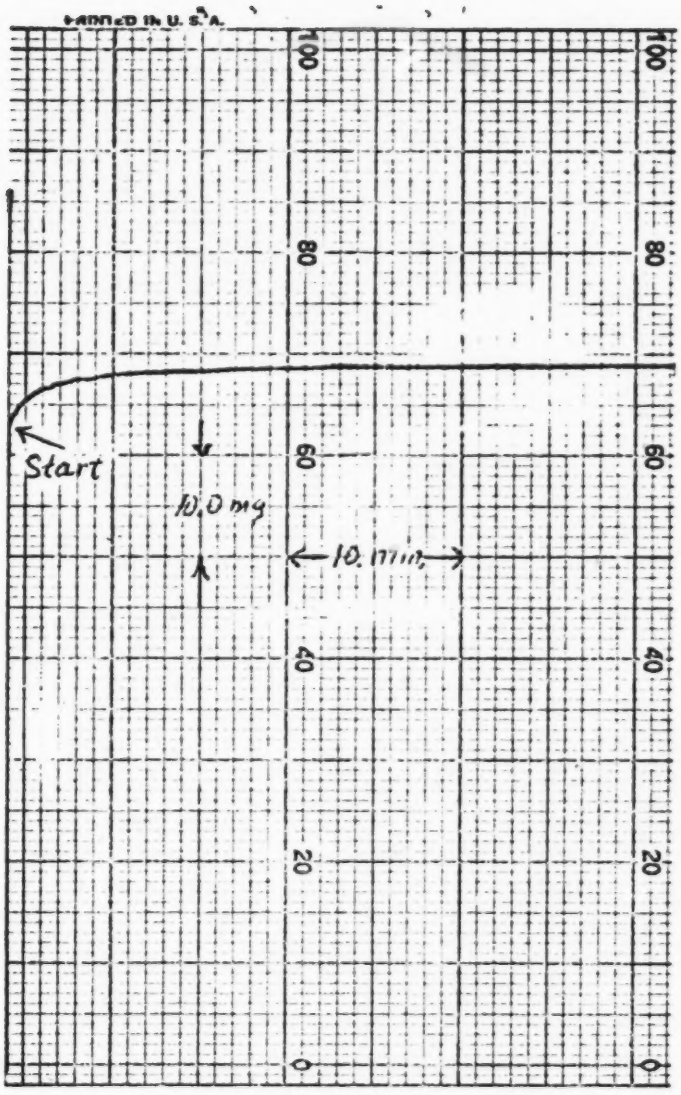

FIGURE 2. EXAMPLE OF LARGE AND RAPID WEIGHT GAIN IN ≈100% RH ATMOSPHERE

Tissuequartz, 1 week in ≈0% RH (Drierite), then put in recording blance having a pan of water. This figure illustrates the large and rapid weight gain of a filter exposed to high humidity.

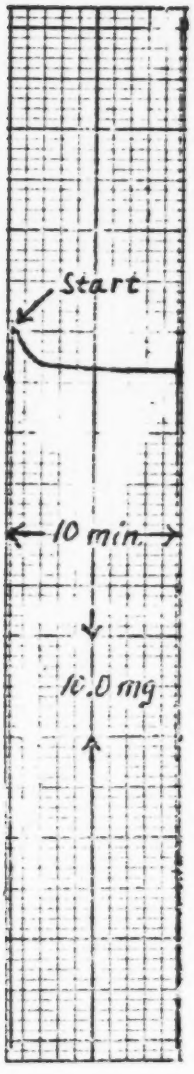

FIGURE 3. EXAMPLE OF WEIGHT LOSS IN ≈0% RH ATMOSPHERE

Tissuequartz, 1 week in ≈100% RH (over H_2O), then put in recording balance having a pan of Drierite. This figure illustrates a small and fairly rapid weight loss to equilibrium.

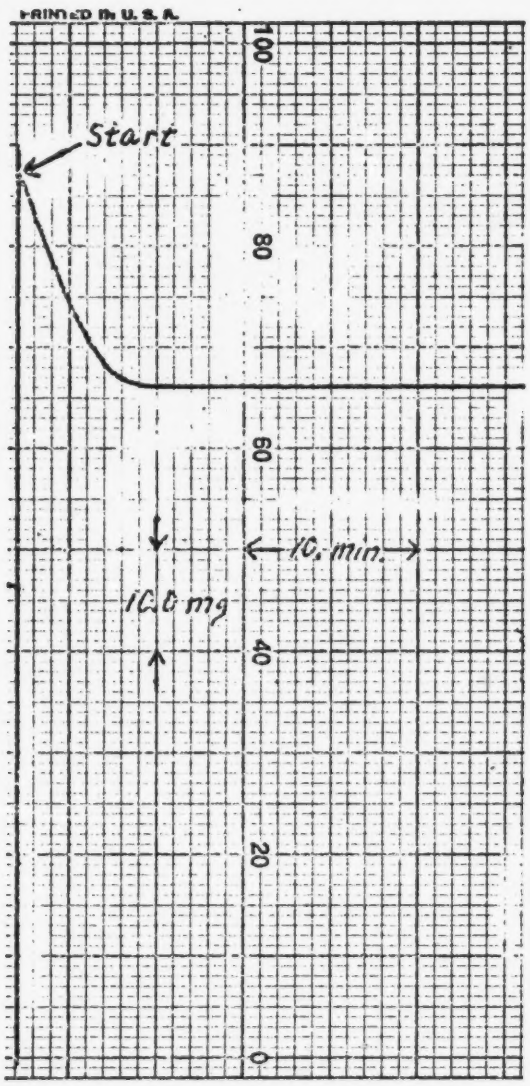

FIGURE 4. EXAMPLE OF WEIGHT LOSS IN ≈0% RH ATMOSPHERE

Whatman GF/B, 1 week in ≈100% RH (over H_2O), then put in recording balance having a pan of Drierite. This figure illustrates a large weight loss over a moderate time period.

FIGURE 5. EXAMPLE OF SLOW AND SMALL WEIGHT GAIN IN ≈100% RH ATMOSPHERE

Whatman GF/A filter, 15 hours in ≈0% RH (Drierite), then put in recording balance having a pan of water. This figure illustrates the (relatively) small and slow but continuing weight gain of a dry filter exposed to high humidity.

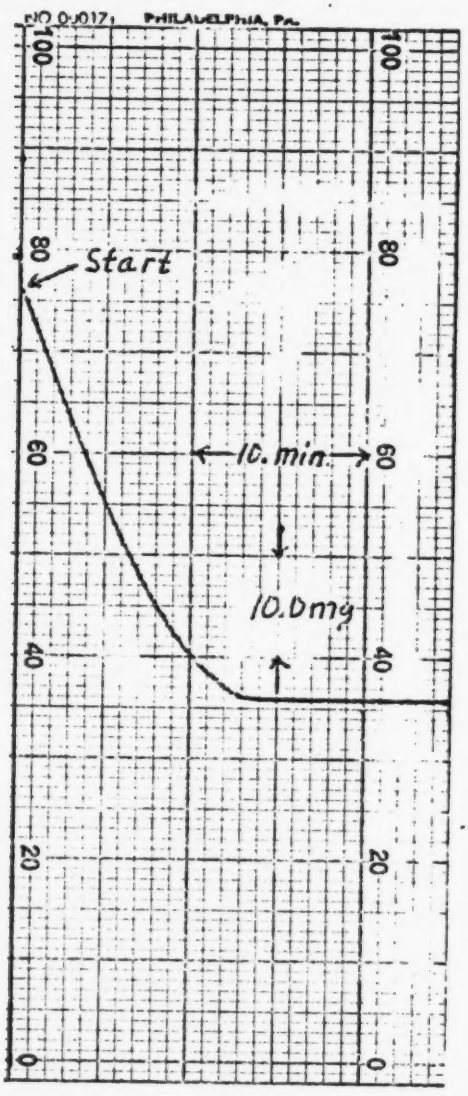

FIGURE 6. WEIGHT LOSS IN ≈0% RH ATMOSPHERE

MSA, 1 week in ≈100% RH (over H_2O), then put in recording balance having a pan of Drierite. This figure illustrates a large and relatively long weight loss to equilibrium.

two Gelman Type A batches where Batch 8170 lost 4.4 mg and Batch 8172 lost 23.8 mg in the humid to dry changes; the relatively low moisture loss (4.9 mg) of the Tissuequartz; and the high loss (30.6 mg) of the MSA filter. In all cases, the excess weight gained at high humidity was lost in less than 15 minutes.

Conclusions Concerning Physical Properties. Within a given type, lot, or box of filters, the variations of physical properties of individual filter disks are small, usually from 1 to 3 percent of the property. Random errors in measurement probably account for some but not all of the variations. In those instances where two boxes or lots of a specific type were checked, the variations between group averages for certain properties appeared larger than the standard deviation for individual measurements (see Table 13, Gelman Type A; Table 16, Whatman Type GF/A; Table 17, several pairs).

Many large differences among the various filter types are apparent from the data in Tables 13 through 17. Some differences, such as thickness, are immediately apparent, even visually. Others, such as humidity response, must be measured. These data were plotted in many ways in an attempt to discover a relationship between some physical property and the measured exhaust particulate collections. No such relationship, consistent among filter types, was found.

It is concluded that physical properties, in and of themselves, do not account for variations observed in exhaust collections. If such a correlation does exist, either it lies with a property not measured, or else the measurements reported here were not sufficiently sensitive or accurate to reveal the correlation.

Chemical Properties

Chemical analyses were made of the filters using optical emission spectrographic, X-ray fluorescence, and combustion techniques. These analyses were made on the entire filter; additionally, optical emission spectrographic analyses were made on the portion of the filter extracted by refluxing a mixture of HCl-HNO_3 through the

filters for 3 hours (standard EPA procedure). The extraction data are of interest primarily in specific applications calling for the acid extraction of collected materials followed by an analysis for specified elements. The direct analysis is of more general interest, especially for applications that do not remove the sample from the filter prior to analysis.

The data in Table 18 show that there are no major differences in metallic (cation) elements among the filters, with the very noticeable exception that the Tissuequartz, made from SiO_2 and not glass, is far cleaner except for Pb and a few other elements. This fact could be a deciding consideration in choosing a suitable filter, if elemental analyses of the exhaust particulate matter is desired.

The presence of an organic binder in the Gelman Type E filter is apparent from the high C and H values.

It has been suggested by EPA that the Zn content correlates with the collection of automobile exhaust particulates. From the data in Table 18 it is not possible to establish a definite correlation. Two filters have very low Zn contents while the other four have much higher amounts averaging about 7.5 mg per 47-mm filter (= 270 $\mu g/cm^2$). However, one of the two filters containing the low zinc content is Tissuequartz and its properties are definitely unlike those of the other filters. Thus the MSA, having a low zinc content, perhaps alone should be compared with the other four filters. On this basis the MSA filter does show a greater auto emission particulate collection. On the other hand, the Whatman GF/B and the Gelman Type E both had high Zn contents, yet gave exhaust collections within 10 percent of the MSA filters.

Study of the Collected Samples

If unused filters yield no striking clues concerning their subsequent behavior as collectors of diluted automobile exhaust, then the analysis of the

TABLE 18. CHEMICAL ANALYSIS OF GLASS FILTERS

(Micrograms of Element Per 47 mm Filter [= 17.34 cm^2])

Element	Whatman GF/A, Box 1 (94 mg)		Whatman GF/B, Box 1 (267 mg)		Gelman Type A, Batch 8170 (151 mg)		Gelman Type E, Batch 8158 (138 mg)		MSA Lot I 702 (107 mg)		Pallfex Tissue Quartz (117 mg) QAO	
	Acid Extract	Direct	Acid Extract	Direct	Acid Extract	Direct	Acid Extract	Direct	Acid Extract	Direct	Acid Extract	Direct
H		83		250		108		910		34		130
Li		3		3		2		2		2		<1
Be	<0.01	<0.5	<0.01	<1	<0.01	<0.6	<0.01	<0.6	<0.01	<0.5	<0.01	<0.5
B		900		2700		1200		1200		1100		1.
C		111		209		256		5800		111		180
N		5		12		11		56		4		27
Na		5500		16,000		7500		7500		11,000		20
Mg		200		250		120		250		750		120
Al		2000		5500		2500		2500		2000		120
Si		Major		Major		Major		Major		Major		Major
P		30		30		20		25		60		8
S		2		5		30		15		40		5
Cl		40		20		5		10		20		20
K		2000		2500		2500		2500		1100		10
Ca		2000		5500		2500		2500		4500		120
Ti	T<0.3	10	T<0.3	30	2.	25	2.	25	T<0.3	2.	T<0.3	6.
V	<0.3	<1.	<0.3	<3.	<0.3	<1.	<0.3	<1.	<0.3	<1.	<0.3	<1.
Cr	<0.3	1.	T<0.3	3.	T<0.3	1.	T<0.3	1.	0.3	2.	T<0.3	<1.
Mn		5		10		6		4		<2		<1.
Fe	6	30	9	80	6	36	17	60	3	55	3	23
Co	<0.3	<1.	<0.3	<3.	<0.3	<1.	<0.3	<1.	<0.3	<1.	<0.3	<1.
Ni	<0.3	<1.	<0.3	<3.	<0.3	<1.	<0.3	<1.	<0.3	<1.	<0.3	<1.
Cu	T<0.1	<1.	T<0.1	<3.	0.1	<1.	0.1	<1.	T<0.1	<1.	4	6.
Zn	Hi	4700	Hi	13,000	Hi	6000	Hi	6200	<3	<10	<3	<10
As	<1	<10	<1	<30	<1	<12	<1	<12	<1	<10	<1	<10
Sr	Hi	50	Hi	130	Hi	60	Hi	60	0.3	20	T<0.1	10
Zr		10		20		6		12		3		2
Mo	<0.1	<1.	<0.1	<3	<0.1	<1	<0.1	<1	<0.1	<1	<0.1	<1
Cd	<0.3	<2	<0.3	<5	<0.3	<2	<0.3	<2	<0.3	<2	<0.3	<2
Sn	<0.3	<2	<0.3	<5	<0.3	<2	<0.3	<2	<0.3	<2	0.4	<2
Sb	<2	<2	<2	<5	<2	<2	<2	<2	<2	<2	<2	<2
Pb	T<1	10	T<1	10	T<1	6	T<1	12	<1	<2	1	25
Bi	<0.3	<1	<0.3	<3	<0.3	<1	<0.3	<1	<0.3	<1	<0.3	<1
Ba		2800		8000		3600		3700		10		1
Total percent by weight of elements other than Si		20.		17.		15.		22.		19.		0.7

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filters after collections might give insight into the causes of variabilities among filters in collection. However, the analyses described in the following sections did not satisfactorily explain the glaring differences in Table 1.

Elemental Analysis. The thirteen MSA filters for which data are given in Table 3, plus two blank MSA filters were analyzed for C and H. Opposite quarters of each filter were taken as duplicate samples for this analysis using a Perkin-Elmer Elemental Analyzer with the sample wrapped in platinum gauze and held in a quartz ladle. The results are shown in Table 19.

The C/H ratios, and the ratios of C to exhaust and H to exhaust were calculated as shown. If gross amounts of carbon were present as elemental carbon, or if much water were present, the C/H ratio would be much different than the approximately 10:1 ratio found in the samples. (Aliphatic hydrocarbons have a C/H ratio of about 12:2 =6, and aromatic hydrocarbons have a ratio of about 12:1 = 12.) The ratio of 1.3 to 1.4 in the blanks suggests residual water.

No obvious correlation can be seen between high exhaust amounts (Column 2) and high C or H values. A correlation would be manifested by a constant ratio in the last two columns, but these ratios are not constant.

Hydrocarbon Analysis. Two sets of filters with exhaust particulate collections were analyzed for hydrocarbons using a extraction-gas chromatographic technique. The first set analyzed is described in Table 2, two or three filters of each type studied in this program. An entire filter was extracted for six hours in CH_2Cl_2 using a micro Soxhlet extractor. The solvent was removed in a Kuderna-Danish concentrator, and the residue was diluted to 100 µl with CH_2Cl_2. Immediately 2 µl of this solution was injected into the chromatographic column. The column, 4 feet of 1/8-inch stainless steel, was packed with 2.5 percent Dexsil (high temperature silicone grease) on Supelcoport. The temperature was programmed,

TABLE 19. CARBON AND HYDROGEN ANALYSIS OF MSA GLASS FILTERS

Filter Location	Gain per filter, μg[a]	C per filter, μg[b]	H per filter, μg[b]	Ratio, C/H	Ratio, C/exhaust[c]	Ratio, H/exhaust[c]
1	345	176	20	8.8	0.51	0.058
2	335	173	20	8.6	0.52	0.060
3	lost	lost	lost	lost	lost	lost
4	451	192	20	9.6	0.43	0.044
5	430	186	19	9.8	0.43	0.044
6	411	137	12	11.4	0.33	0.029
7	407	141	14	10.0	0.35	0.034
8	501	150	13	11.5	0.30	0.026
9	438	163	18	9.1	0.37	0.041
10	347	163	18	9.1	0.47	0.052
11	422	153	14	10.1	0.36	0.033
12	300	lost	lost	lost	lost	lost
13	544	199	28	7.1	0.37	0.051
Average	411	168	17.7	9.6	0.41	0.043
Blank	-16	35	26	1.3	--	--
Blank	-23	38	26	1.4	--	--
Average deviation	53[a]	21	4	--	0.072	0.012
Percent Ave. dev.	12.9[a]	12.6	26.1	--	17.5	28.1

(a) Data from Table 3.

(b) Average of values from two quarters. Net (blank subtracted) value.

(c) Exhaust = Gain per filter, column 2.

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starting at 50 C, at + 20 C per minute to a maximum of 300 C. Dry nitrogen was the carrier gas, and the detector was a flame ionization unit. These conditions were selected, after some experimentation, to give a partially resolved envelope containing most of the heavier hydrocarbons. The envelope was broad, starting at about 6 minutes and ending at about 16 minutes, with many partially resolved peaks superimposed. Comparing the sample chromatograms with standard straight chain hydrocarbons, the sample elution covered the approximate carbon number range of C_{16} through C_{38}. Most of the aliphatic, aromatic, saturated, unsaturated, and polynuclear compounds would be represented within the broad envelope; highly polar compounds such as carboxylic acids would not be detected in this manner.

The analyses were repeated later by evaporating the CH_2Cl_2 solvent, then rediluting to 100 µl and repeating the injection and elution. The data from both analyses are given in Table 20.

Rather clearly, the data in Table 20 are not sufficiently precise to permit conclusions to be drawn. No blanks were run except for the Tissuequartz filters and this lack further contributes to an overall uncertainty. The method for determining total hydrocarbons needs further refinement if this aspect of filter variability is to be explored.

The MSA filters with exhaust particulates, for which data are given in Tables 3 and 19, were analyzed for total hydrocarbons using the extraction - chromatography method described above. In this case one quarter of the filter was extracted; two injections, elutions, and area measurements were made for each filter. The hydrocarbon data, and pertinent data from Tables 3 and 19, are shown in Table 21.

The important fact in Table 21 is that the hydrocarbon blank is essentially the same as the average hydrocarbon value found in the filters with exhaust particulates. (Note that such was not the case for Tissuequartz, Table 20.) Any future work must

TABLE 20. HYDROCARBON CONTENT OF EXHAUST COLLECTIONS ON GLASS FILTERS

Filter Type[a]	Filter Location[a]	Gain per filter, μg [a]	Hydrocarbon[b] Run 1	Hydrocarbon[b] Run 2	Average
Whatman GF/A	10	288	1.91	2.65	1.98
Whatman GF/A	6	255	1.48	1.90	
Whatman GF/B	7	421	3.17	2.98	3.64
Whatman GF/B	8	890	3.82	4.59	
Gelman Type A	4	1,403	2.92	1.82	2.38
Gelman Type A	3	687	2.26	2.50	
Gelman Type E	2	419	3.45	2.42	3.31
Gelman Type E	5	416	3.61	3.76	
MSA	1	369	2.46	3.60	
MSA	13	520	3.35	3.14	3.09
MSA	12	295	3.11	2.87	
Tissuequartz	9	55	3.50	3.93	3.72
Tissuequartz	11	180	3.39	4.07	0.66
Blank	Blank	--	0.73	0.60	
Average					

(a) Data are from Table 7.
(b) Arbitrary units (square inches under elution peak).

TABLE 21. HYDROCARBON CONTENT OF EXHAUST COLLECTIONS ON MSA GLASS FILTERS.

Filter Location	Gain per Filter, µg(a)	C per Filter, µg (b)	H per Filter, µg (b)	HC per Filter (c)	Ratio HC/Exhaust(d)
1	345	176	20	1.8	0.0052
2	335	173	20	2.8	0.0084
3	lost	--	--	--	--
4	451	192	20	2.0	0.0044
5	430	186	19	2.8	0.0065
6	411	137	12	2.8	0.0068
7	407	141	14	2.4	0.0059
8	501	150	13	3.2	0.0064
9	438	163	18	3.1	0.0071
10	347	163	18	3.3	0.0095
11	422	153	14	2.6	0.0062
12	300	lost	--	--	--
13	544	199	28	4.4	0.0081
Average	411	168	17.7	2.83	0.0068
Average deviation	53	21	4	0.47	0.0011
Percent Avg. Dev.	12.9	12.6	26.1	16.9	16.2
Blank	-16	35	26	3.0	--
Blank	-23	38	26	2.4	--

(a) From Table 3.
(b) From Table 19.
(c) Arbitrary units (square inches under peak). Average of two determinations, not corrected for blank.
(d) Exhaust = Gain per filter, Column 2.

establish unequivocally the relationship of the blank and the sample. Is the blank merely a reagent and column blank, or is it truly a filter blank? If it is a filter blank, then is the extraction-chromatography method really detecting any hydrocarbons in the sample? Are there, in fact, any hydrocarbons there to detect? These questions must be answered before any conclusions can be made concerning the role of hydrocarbons in the observed particulate weight.

If the question of blanks is ignored, and only the relationship between the measured hydrocarbon peak and the observed weight is examined, a slight correlation may exist. Certainly the data should be subjected to rigorous statistical analysis; these data, and those in Tables 19 and 20, were not considered sufficiently precise or comprehensive to warrant such analyses.

Thermogravimetric Analysis. If part or all the observed variations in the weight of collected automobile exhaust particulates are caused by adsorbed or condensed hydrocarbons, which normally would have passed through the filter as a gas but were retained in varying amounts, then it should be possible to drive off these extraneous substances by heat. This hypothesis was tested by performing thermogravimetric analysis (TGA) on three of the MSA filters with exhaust particulates (Tables 3, 19, and 21) and two blank MSA filters. For the TGA runs, one-fourth of a 47-mm-diameter filter was taken. This portion was placed in the pan of the TGA, which had been carefully calibrated and tared in the appropriate weight range. The chamber was evacuated to the 10^{-5} torr range using rotary and oil diffusion pumps, and the steady state weight of the filter was obtained. Heating at the rate of 4 C per minute was then begun, using a controlled resistance heater surrounding the pan and sample leg of the TGA unit. Weight loss was recorded on a stripchart recorder. The maximum temperature of 490 to 500 C was reached in about two hours. At the end of the heating period the furnace was removed and the leg allowed to cool to ambient temperature, at which point the steady state weight was again observed.

The two blank samples gave remarkable weight losses, 0.0890 and 0.0900 mg from starting weights of 27.2072 and 28.6584 mg, respectively. The blank weight loss for these MSA filters corresponds to about 0.35 mg per 47-mm filter, nearly the same as the weight loss found at ambient temperature when MSA filters were transferred from humid to dry conditions (Table 17). The two types of weight loss may not be similar, however. At ambient temperature and pressure the loss of water was essentially complete after about 20 to 25 minutes whereas the loss of weight in the TGA experiments was still occurring after 2 hours. Thus, the similarity in weight losses in the humidity-ambient temperature and the TGA experiments probably is coincidental.

Similar TGA runs were made using quarter-filter segments from filters 9, 10, and 13 (Tables 3, 19, and 21). These showed weight losses of 0.540, 0.628, and 1.160 mg, respectively, calculated on an entire 47-mm-diameter filter. If the average blank value of 0.358 mg is subtracted from each sample weight loss, the net losses are 0.182, 0.270, and 0.802 mg, respectively. The first two values are within reason considering the weights of particulate matter collected, but the value from filter 13 is about 50 percent more than the total weight of sample.

Thus, the TGA data present a confusing picture. On the one hand the blank runs and the runs for two samples are plausible. On the other hand the run for Sample 13 is not logical, and casts doubt on the validity of the technique employed.

Conclusions Concerning Analysis of Collected Samples. The analytical steps failed to discover the cause of differences observed among collected exhaust samples. The approach taken in this program was to attempt to find a single component of the samples to account for the variations. Perhaps this approach is still valid, and the search should continue. An alternative approach suggests itself, however. Perhaps the weight variations are not caused by a single event, such as hydrocarbon

adsorption, but rather are a manifestation of many unrelated events whose summation produces the observed variations. If the latter be true, then future work should stress statistical studies to discover the more subtle relationships among variables. If such relationships can be identified, then means can be devised to reduce the dependency of the exhaust collection upon these variables. Suggestions for additional studies along both lines are presented in the future work section of this report.

Calibration of Exhaust Dilution Tunnel

The dilution tunnel used in this program was constructed for a project studying the fate of automobile exhaust particulate matter in the atmosphere, sponsored by the Coordinating Research Council and Environmental Protection Agency. The tunnel is about 2 feet in diameter and about 36 feet long. About 30 feet from the dilution point are located 13 sampling ports arranged in a vertical and a horizontal line, 3 ports per quadrant plus 1 in the center. Each port leads to a fitting outside the tunnel; a filter holder with a critical flow orifice is attached to each fitting, and the exit sides of the filters are connected via a manifold to a large mechanical vacuum pump. The location of the inlet ports was shown in Figure 1.

It is important to be certain that each of the 13 sampling ports is equivalent to all the others. If the ports would not sample representative fractions of the diluted exhaust, i.e., if the exhaust stream preferentially followed a limited path through the tunnel, then comparisons among filters sampling the various ports with the assumption that all sampling positions are identical would not be valid.

The uniformity of distribution of the diluted exhaust was checked by injecting a fluorescent dye aerosol into the exhaust stream before dilution, catching the dye on the 13 filters, and measuring the quantity by nondispersive fluorimetry. The uniformity of the critical flow orifices is checked simultaneously by this experiment. An aerosol can ("spray paint" type) was prepared containing dye, toluene solvent, and Freon 12 propellant. The dye was injected into the exhaust stream through a small copper tube whose exit axis was concentric with the automobile exhaust pipe. With the automobile running on the chassis dynamometer at a steady 35 mph and 3 hp, the contents of the aerosol can was slowly injected into the exhaust. Simultaneously with the filter collections, a cascade impactor collection was made to determine the aerosol particle size distribution.

The uniformity of distribution of the aerosol on the filters is given in Table 22. It is clear that the variations are minor and that the exhaust is mixed essentially completely throughout the cross section of the tunnel. The percent coefficient of variation is less than that found for any other parameter of the filter materials measured in this study. This fact shows that flow variations within the tunnel are not a major source of filter-to-filter variations.

One filter holder (location 12) was found to have a 1.0 cfm critical orifice, approximately twice the 0.5 cfm orifices of the other 12. Data from this holder in this report have been corrected by a factor of 0.5 when possible.

TABLE 22. DISTRIBUTION OF DYE AEROSOL AT REPLICATE SAMPLING SITES

Filter Location[(a)]	Photometer Reading Arbitrary Units
1	80.5
2	81.2
3	80.5
4	78.3
5	83.0
6	79.4
7	85.6
8	78.0
9	76.4
10	85.5
11	74.0
12	75.5(b)
13	82.3

(a) See Figure 1 for location diagram

(b) Corrected - see text

$\sigma = \sqrt{\frac{\Sigma(\bar{R} - R)^2}{n-1}}$, where R is the arbitrary photometer reading (=3.59)

Percent coefficient of variation $\nu = \frac{\sigma}{\bar{R}} \times 100$ (=4.48)

In those cases when a correction might not be valid, the data were discarded as "lost". The improper critical flow orifice was replaced with the correct size before making the collections reported in Tables 4, 5, and 6 and 8 through 12.

Particle size distribution of the aerosol was determined by drawing a portion of the diluted exhaust through a Battelle cascade impactor backed by a glass fiber filter. The amount of dye impacted on each stage of the impactor and caught by the backing filter is given in Table 23, which shows that the major portion of the aerosol is less than 1 μm. A plot of the cumulative percent of each size is shown in Figure 7.

CONCLUSIONS AND RECOMMENDATIONS

Many conclusions may be drawn from the data presented in this report; some conclusions have been presented at the end of each major section.

Two primary conclusions are apparent. First, real differences exist and can be measured among the weights of diluted automobile exhaust collected on different types of filters; similar differences are not apparent when particulate matter from ambient air is collected. Second, no single factor, or combination of factors, has been identified as the cause of these variations. Many causes, both within the filters themselves and also within the collected samples, were examined as possible causative factors. Although some trends and possible relationships might be postulated from the data, these cause-effect relationships are tenuous at best; more data are needed, in order to establish definite links.

Recommendations are presented in the concluding section.

FUTURE WORK

The key to the successful search for the causes of weight variations in exhaust collections may ultimately lie in statistics. The search for a single variable responsible for the weight differences, either in the filter or

TABLE 23. SIZE DISTRIBUTION OF DYE AEROSOL

Stage Number	Effective Stoke's Diameter, μm	Percent of Total on Stage	Cumulative Percent
Filter	0.25	76.8	76.8
7	0.25	10.1	86.9
6	0.50	2.3	89.2
5	1.0	3.1	92.3
4	2.0	4.1	96.4
3	4.0	2.5	98.9
2(a)	8.0	1.1	100.0

(a) Stage 1 (16 μm) not used in cascade impactor assembly.

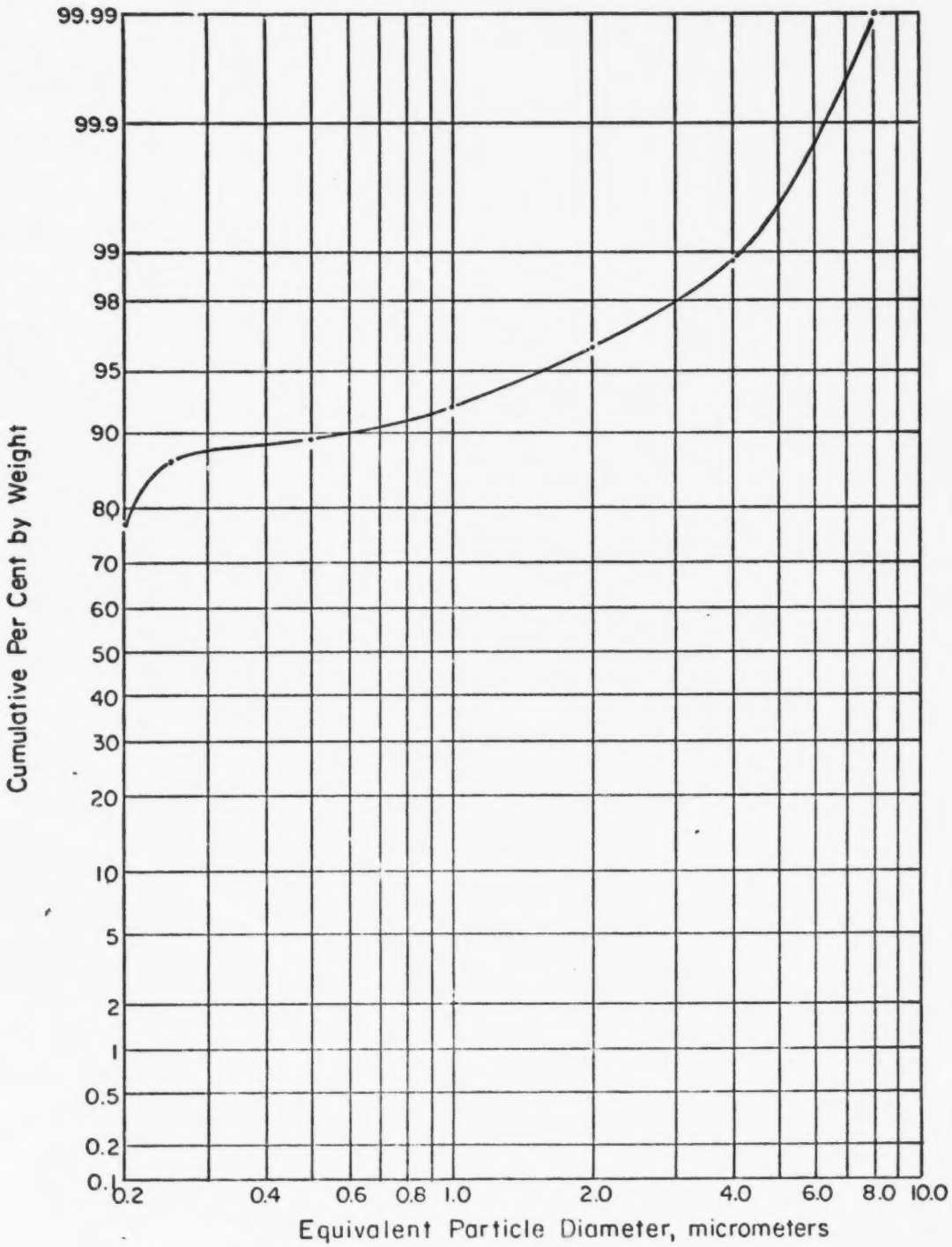

FIGURE 7. PARTICLE SIZE DISTRIBUTION OF AEROSOL USED TO CALIBRATE DILUTION TUNNEL

the sample, did not succeed. While not dismissing the possibility that that single variable has been overlooked, it seems more probable that many factors have a cumulative effect. If so then it follows that the number of observations should be large enough to minimize the impact of wild or false data and to allow trends to be seen. Of course the cost of acquiring large amounts of data can escalate beyond reason if the experimental work is not carefully planned and designed statistically so that the data can be interpreted meaningfully.

The search for variability relationships should be confined to intertype studies rather than intratype studies. For the initial studies, the variability among filters of a given type should be treated as a fact, not investigated. Intratype variability properly follows the successful identification of variability among different types of filters.

Translated into specific steps, these broad suggestions lead to the following program.

(1) Select two to four types of filters for intensive study. The Whatman GF/A and the MSA types should be included since they contain two distinctly different concentrations of zinc.

(2) Make repetitive simultaneous exhaust collections using the selected types, varying controllable parameters one at a time.

(a) Face velocity at filter.

(b) Filter holder configuration.

(c) Dilution of exhaust.

(d) Humidity and temperature at collection point.

(e) Ambient humidity during tare and gross weighings.

It is realized some of these variables are mutually dependent.

(3) Statistically analyze the data and attempt to correlate observed weights with the variables.

(4) If correlations are found, analyze several samples from the extreme ends of the range, e.g., some from low and some from high face velocities if that is a correlating variable.

(5) Devise experimental conditions to measure the exit stream from each filter. This could involve monitors placed in the volumes immediately following each filter to measure water vapor, hydrocarbons, or any untrapped particulate species. Alternatively, backup filters and/or impingers could be used to trap material escaping the first filter.

(6) Experiment with predrying beds as has been done in some ambient air particulate studies. It is recognized that such beds may alter the chemical composition of the exhaust and introduce another variable whose effect will be very difficult to measure.

(7) It may prove desirable to alter the exhaust characteristics, as by running the engine too rich, to cause exaggerated collection errors. This approach has the severe disadvantage of yielding high weights of particulates that may swamp or obscure the smaller but significant variations now observed.

(8) Refine analytical methods to determine specific components. This task is not incompatible with the hypothesis that more than one cause of variation is responsible, since each individual cause eventually should be studied. Because water and hydrocarbons remain the most probable, but unproven, causes of variations, better means are needed to determine them. Modified extraction - chromatographic techniques should be developed for hydrocarbons; perhaps it will become necessary to separate the hydrocarbons into classes, even individual compounds. For water, a modified TGA technique is envisioned, wherein the amount of water evolved as a function of temperature is measured, not the weight loss.

If these experiments are successful in identifying the causes of variations among the few types of filters, the next step is to determine if the same causes also affect other filter types. Paired, statistically valid experiments should be able to establish whether or not the findings from the first filter types are applicable to all other types. If as expected the first results are applicable to other filter types, the variables causing weight differences among filter types can be summarized as generally applicable, with statistical limits given for the average effect of each variable.

When that phase is completed, the next task is to define statistical limits for variations within a given filter type. Many of these data will have been assembled during the other studies, but should be retabulated to stress intratype variability.